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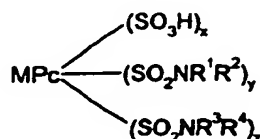
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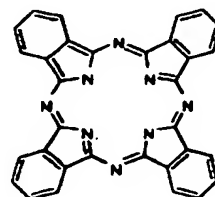
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(54) Title: PHTHALOCYANINE COMPOUNDS, INK COMPOSITIONS COMPRISING SAID COMPOUNDS, AND PRINTING PROCESS THEREWITH



(1)



(2)

(57) Abstract: A process for forming an image on a substrate comprising applying a composition comprising: (a) a compound of Formula (1) and salts thereof, wherein: M is Cu or Ni; Pc represents a phthalocyanine nucleus of Formula (2); R¹, R² and R³ independently are H or optionally substituted C₁₋₄alkyl; R⁴ is optionally substituted C₁₋₄-hydroxyalkyl; x is greater than 0 and less than 1.8; y and z are both greater than 0; and the sum of (x+y+z) is 2.4 to 4.5; and (b) a liquid medium: thereto by means of an ink jet printer. Also compositions, inks, compounds and ink jet printer cartridges.

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PHTHALOCYANINE COMPOUNDS, INK COMPOSITIONS COMPRISING SAID COMPOUNDS, AND
PRINTING PROCESS THEREWITH

This invention relates to a an ink-jet printing process, to compositions and inks suitable for use in this process, to novel compounds from which these compositions and inks may be prepared, to printed substrates and to ink-jet printer cartridges.

5 Ink-jet printing is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for dyes and inks used in ink-jet printing. For example they desirably provide sharp, non-feathered images having good water, light and ozone fastness and optical density. The inks are often required to
10 dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink-jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate that could block the fine printer nozzles.

Dyes containing a single copper phthalocyanine group and their use in ink-jet
15 printing are known. For example, C.I. Direct Blue 199 and C.I. Direct Blue 86 are used as colorants in commercial ink-jet printing inks. There are also newer phthalocyanines such as those described in US 6,149,722. However, there is a continuing need to provide colorants having superior properties in ink-jet printing inks.

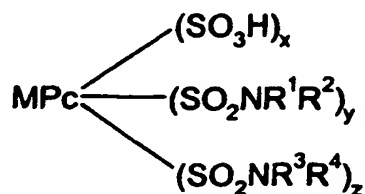
A particular problem for photorealistic quality printing is that of permanence, that is
20 the ability of the colourants used in producing a photographic print to retain their colour properties over a number of years. A key factor contributing to the poor permanence of prints is the quenching of printed colorants by atmospheric pollutants, such as ozone.

We have now found that certain cyan colorants when used in ink-jet printing
25 processes yield prints with improved permanence and especially improved ozone-fastness.

Thus, according to the present invention there is provided a process for forming an image on a substrate comprising applying a composition which comprises:

(a) a compound of Formula (1) and salts thereof:

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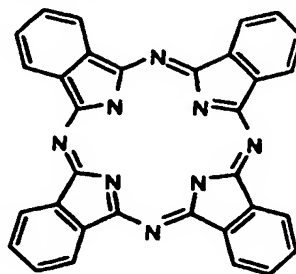


Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus of Formula (2);



Formula (2)

R^1 , R^2 and R^3 independently are H or optionally substituted C_{1-4} alkyl;

R^4 is optionally substituted C_{1-4} -hydroxyalkyl;

x is greater than 0 and less than 1.8;

y and z are both greater than 0; and

the sum of (x+y+z) is 2.4 to 4.5; and

(b) a liquid medium:

thereto by means of an ink-jet printer.

The ink-jet printer preferably applies the composition to the substrate in the form of droplets that are ejected through a small orifice onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected from the orifice in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink-jet printers the oscillation of a small crystal causes ejection of the ink from the orifice. Alternately the ink can be ejected by an electromechanical actuator connected to a moveable paddle or plunger, for example as described in International Patent Application WO 00/48938 and International Patent Application WO 00/55089.

The substrate is preferably paper, plastic, textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, treated or coated papers which may have an acid, alkaline or neutral character.

Photographic quality paper is particularly preferred.

Preferably in the compound of Formula (1) R^1 , R^2 and R^3 independently are H or methyl, more preferably in the compound of Formula (1) R^1 , R^2 and R^3 are all H.

In the compound of Formula (1) R^4 may comprise more than 1 hydroxy group, although preferably R^4 comprises a single hydroxy.

Preferably in the compound of Formula (1) R^4 is unsubstituted C_{1-4} -hydroxyalkyl, more preferably C_2 -hydroxyalkyl.

Preferred optional substituents which may be present on R^1 , R^2 , R^3 and R^4 are independently selected from: optionally substituted alkoxy (preferably C_{1-4} -alkoxy), optionally substituted aryl (preferably phenyl), optionally substituted aryloxy (preferably phenoxy), optionally substituted heterocyclic, polyalkylene oxide (preferably polyethylene oxide or polypropylene oxide), carboxy, phosphato, sulpho, nitro, cyano, halo, ureido, $-SO_2F$, hydroxy, ester, $-NR^5R^6$, $-COR^5$, $-CONR^5R^6$, $-NHCOR^5$, carboxyester, sulphone, and $-SO_2NR^5R^6$, wherein R^5 and R^6 are each independently H or optionally substituted alkyl (especially C_{1-4} -alkyl). Optional substituents for any of the substituents described for R^1 , R^2 , R^3 and R^4 may be selected from the same list of substituents.

It is especially preferred that in the compound of Formula (1) that R^1 , R^2 and R^3 are all H and R^4 is C_{1-4} -hydroxyalkyl, particularly $-CH_2CH_2OH$.

Preferably in the compound of Formula (1) x is greater than 0 and less than 1.5, more preferably x is greater than 0 and less than 1.2, especially x is greater than 0.05 and less than 1.0, more especially x is greater than 0.05 and less than 0.8 and particularly x is greater than 0.05 and less than 0.5.

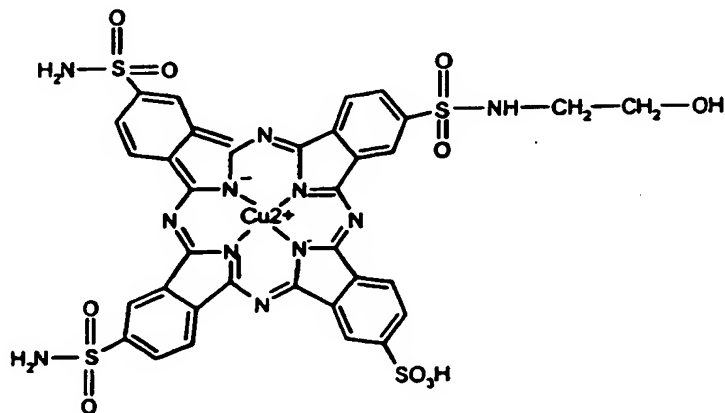
Preferably in the compound of Formula (1) the sum of $y + z$ is in the range of from 2.4 to 4.2, more preferably 2.7 to 4.1.

In the compound of Formula (1) the sum of $(x + y + z)$ is preferably 3.5 to 4.5, more preferably the sum of $(x + y + z)$ is 3.8 to 4.2 and especially the sum of $(x + y + z)$ is 4.0.

The values for x , y and z in compounds of Formula (1) all represent statistical averages.

The substituents represented by x , y and z may be present on any susceptible position on the phthalocyanine ring system.

In one preferred embodiment it is provided that the compound of Formula (1) is not of formula



Acid or basic groups on the compounds of Formula (1), particularly acid groups, are preferably in the form of a salt. Thus, the Formulae shown herein include the compounds in free acid and in salt form.

5 Preferred salts are alkali metal salts, especially lithium, sodium and potassium, ammonium and substituted ammonium salts (including quaternary amines such as $((\text{CH}_3)_4\text{N}^+)$ and mixtures thereof. Especially preferred are salts with sodium, lithium, ammonia and volatile amines, more especially sodium salts. The compounds may be converted into a salt using known techniques.

10 The compounds of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present invention.

The compounds of Formula (1) may be prepared by condensing copper or nickel phthalocyanine carrying sulphonyl chloride groups and sulphonic acid groups with compounds of formula HNR^1R^2 and HNR^3R^4 wherein R^1 , R^2 , R^3 and R^4 are as
15 hereinbefore defined. Many compounds of formula HNR^1R^2 and HNR^3R^4 are commercially available, for example ammonia and ethanolamine, other made be readily prepared by a person of ordinary skill. The condensation is preferably performed in water at a pH above 7. Typically the condensation is performed at a temperature of 30 to 70°C and the condensation is usually complete in less than 24 hours. The compounds of
20 formula HNR^1R^2 and HNR^3R^4 may be used as a mixture or condensed sequentially with the said phthalocyanine compound.

Copper and nickel phthalocyanines carrying sulphonyl chloride groups and optionally sulphonic acid groups may be prepared by chlorosulphonating copper or nickel phthalocyanine, e.g. using chlorosulphonic acid and optionally a chlorinating agent (e.g.
25 POCl_3 , PCl_5 or thionylchloride).

Preferred compositions comprise:

- (a) from 0.01 to 30 parts of a compound of Formula (1); and
- (b) from 70 to 99.99 parts of a liquid medium.

30 The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates that may be used to prepare more dilute inks and
35 reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media include water, a mixture of water and organic solvent and organic solvent free from water.

When the medium comprises a mixture of water and organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

5 It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 10 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; 15 20 cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulfoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, 25 ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

30 Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore-described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, 35 aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH₂Cl₂; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the compound in the liquid medium. Examples of suitable polar solvents include C₁₋₄-alcohols.

5 In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) and/or an alcohol (especially a C₁₋₄-alkanol, more especially ethanol or propanol).

10 The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected that gives good control over the drying characteristics and storage stability of the ink.

15 Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

The liquid media may also contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or non-ionic.

20 Although not usually necessary, further colorants may be added to the composition to modify the shade and performance properties. Examples of such colorants include C.I.Direct Yellow 86, 132, 142 and 173; C.I.Direct Blue 199, and 307; C.I.Food Black 2; C.I.Direct Black 168 and 195; C.I.Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark
25 International. Addition of such further dyes can increase overall solubility leading to less kogation (nozzle blockage) for the resultant ink.

30 So that the compositions do not block the nozzles of the ink jet printer in use they are preferably prepared using high purity ingredients and/or by purifying the composition after it has been prepared. Suitable purification techniques are well known, e.g. ultrafiltration, reverse osmosis, ion exchange and combinations thereof (either before or after they are incorporated in a composition according to the present invention). This purification results in the removal of substantially all of the inorganic salts and by-products resulting from its synthesis. Such purification assists in the preparation of a low viscosity aqueous solution suitable for use in an ink-jet printer.

35 Preferably the composition has a viscosity of less than 20 cP, more preferably less than 10 cP, especially less than 5 cP, at 25°C. These low viscosity compositions are particularly well suited for application to substrates by means of ink-jet printers.

40 Preferably the composition contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of divalent and trivalent metal ions (other than any divalent and trivalent metal ions bound to a

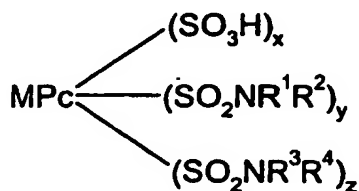
component of the composition). Free divalent and trivalent metals can form insoluble complexes on storage that could block the ink-jet printer nozzles.

Preferably the composition has been filtered through a filter having a mean pore size below $10\mu\text{m}$, more preferably below $3\mu\text{m}$, especially below $2\mu\text{m}$, more especially below $1\mu\text{m}$. This filtration removes particulate matter that could otherwise block the fine nozzles found in many ink-jet printers.

Preferably the composition contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of halide ions. High levels of halide ions can cause detrimental effects such as, for example, corrosion of metal parts in the ink-jet printer heads.

A second aspect of the invention provides a composition comprising:

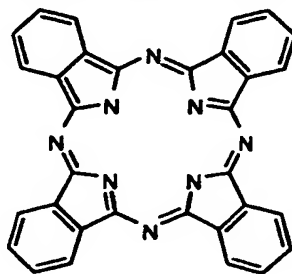
(a) a compound of Formula (1) and salts thereof:



Formula (1)

wherein:

M is Cu or Ni;
Pc represents a phthalocyanine nucleus of Formula (2);



Formula (2)

R^1 , R^2 and R^3 independently are H or optionally substituted C_{1-4} alkyl;
 R^4 is optionally substituted C_{1-4} -hydroxyalkyl;
 x is greater than 0 and less than 1.8;
 y and z are both greater than 0; and
the sum of $(x+y+z)$ is 2.4 to 4.5; and

(b) a liquid medium which comprises water and an organic solvent or an organic solvent free from water.

Preferred compositions are as described in the first aspect of the invention.

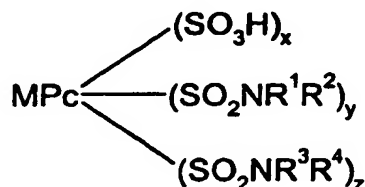
Preferences for the compounds of Formula (1) are as described and preferred in the first aspect of the invention.

The organic solvent in the mixture of water and organic solvent is as preferred in the first aspect of the invention.

The organic solvent free from water is as preferred in the first aspect of the invention.

It is particularly preferred that the composition according to the second aspect of the invention is an ink-jet printing ink or a liquid dye concentrate. Concentrates are useful as a means for transporting colorant and so minimising costs associated with drying the dye and transporting excess liquid.

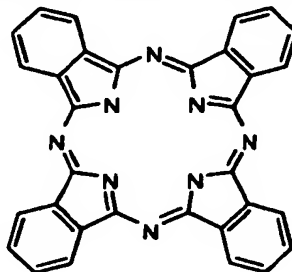
A third aspect of the present invention provides a compound of Formula (1) and salts thereof:



Formula (1)

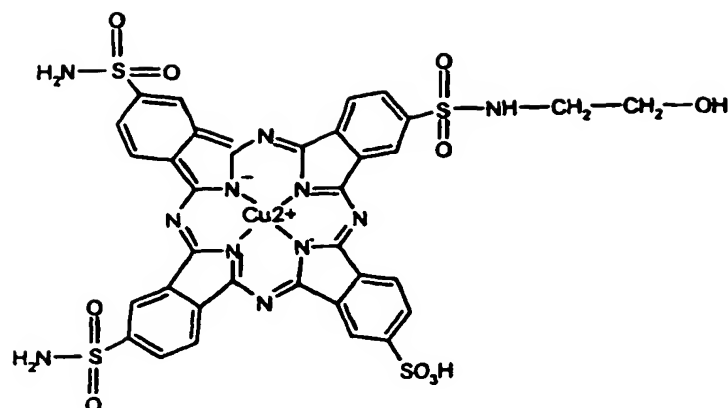
wherein:

M is Cu or Ni;
Pc represents a phthalocyanine nucleus of Formula (2);



Formula (2)

R^1 , R^2 and R^3 independently are H or optionally substituted C_{1-4} alkyl;
 R^4 is optionally substituted C_{1-4} -hydroxyalkyl;
 x is greater than 0 and less than 1.8;
 y and z are both greater than 0; and
the sum of $(x+y+z)$ is 2.4 to 4.5;
provided that the compound of Formula (1) is not of formula



Compounds of Formula (1) are as preferred in the first aspect of the invention.

The compounds of Formula (1) may be prepared as described in the first aspect of the invention.

5 The compounds of Formula (1) have attractive, strong cyan shades and are valuable colorants for use in the preparation of ink-jet printing inks. They benefit from a good balance of solubility, storage stability and fastness to water and light. In particular they display excellent light and ozone fastness. Furthermore they may be prepared from cheap intermediates, avoiding the complexity and expense which is involved in manufacturing
10 some of the more elaborate phthalocyanines.

A fourth aspect of the invention provides a composition which comprises a compound of Formula (1) according to the third aspect of the invention and a liquid medium. Preferred liquid media include water, a mixture of water and organic solvent and organic solvent free from water as described in the first aspect of the invention.

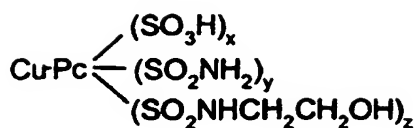
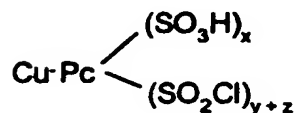
15 A fifth aspect of the present invention provides paper, plastic, textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper more especially plain, coated or treated papers and particularly photographic quality paper printed by means of a process according to the first aspect of the invention, with a composition according to the second or fourth aspects of the invention or with a compound
20 according to the third aspect of the invention.

A sixth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in the second or fourth aspects of the present invention.

25 The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1

Preparation of the following dye wherein x is 0.8 and (y + z) is 3.2:

Stage 1Preparation of:

5

Copper phthalocyanine (118.7g; molar ratio 1) was added in portions to a mixture of stirred chlorosulphonic acid (310 ml; molar ratio 23) and phosphorous oxychloride (37.8 ml; molar ratio 2) while keeping the temperature in the range of 50 to 60 °C. The mixture was heated gradually to 140°C, and kept at that temperature, with stirring, for 3 hours. The reaction mixture was then poured onto a mixture of ice (3kg), water (1400ml) and sodium chloride (160g). The precipitate which formed was collected by filtration at reduced pressure and washed with 3% brine (500 ml) before being used in Stage 2.

15 Stage 2Preparation of title dye:

Water (2 litre), ethanolamine (24.6 g, molar ratio 2) and 35% ammonia solution (20g; molar ratio 2) were mixed in a 5 litre beaker and then placed in an ice bath (pH = 11.5, temperature 8° C). The phthalocyanine sulphonyl chloride paste (molar ratio 1), resulting from stage 1 above, was slowly added to the mixture while the temperature was kept below 5° C and the pH was maintained at pH 8 by the addition of 10% v/v sodium hydroxide. The reaction mixture was left overnight at room temperature and then heated at 40°C for 4 hours. Sodium chloride (50% w/v) was added and the resultant precipitate was collected by filtration at reduced pressure and desalinated by dialysis to obtain the title dye wherein x is 0.8 and (y + z) is 3.2.

25

Examples 2 to 9

Example 1 was repeated except that the molar ratios of POCl₃, ethanolamine and ammonia were as shown in Table 1.

30

Examples 10 to 16Stage 1

35

The method of Example 1, stage 1, was repeated except that the molar ratio of POCl₃ used in each example was as shown in Table 1.

Stage 2

Water (1 litre) and ethanolamine (12g, molar ratio 1) were mixed and then placed in an ice bath. The phthalocyanine sulphonyl chloride pastes (molar ratio 1), prepared as described in stage 1 were slowly added to the mixture while the temperature was kept below 5° C and the pH was maintained at pH 8 by the addition of 10% v/v. ammonia solution. The reaction mixture was left overnight at room temperature and then heated at 40°C for 4 hours. Sodium chloride (20% w/v) was added and the resultant precipitate was collected by filtration at reduced pressure and desalinated by dialysis to obtain the phthalocyanine dyes described in Examples 10 to 16 of Table 1 below.

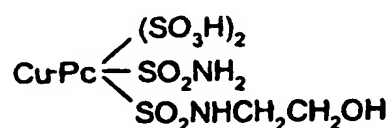
Table 1

Example	POCl ₃ (molar ratio)	Ethanolamine (molar ratio)	Ammonia (molar ratio)	x	y + z
2	2	4	2	0.1	4.0
3	2	6	2	0.1	4.0
4	2	2	4	1.1	3.0
5	2	2	6	1.0	3.0
6	2.5	2	4	0.4	3.4
7	2.5	4	2	0.2	3.6
8	2.5	2	6	0.2	3.4
9	2.5	2	2	0.6	3.2
10	1.5	1	AR	1.3	2.8
11	2	1	AR	0.8	3.2
12	2.5	1	AR	1.4	2.6
13	3	1	AR	0.8	3.2
14	3.5	1	AR	0.4	3.6
15	3.8	1	AR	0.4	3.8
16	1	1	AR	0.7	3.4

AR – as required to adjust the pH is step (b) to pH 8.0.

Comparative Example

The phthalocyanine dye:



was prepared as described in Example 1 of US 6,149,722 which preparation is incorporated herein by reference.

Examples 17 to 33

5 Preparation of Inks 1 to 16

10 The compounds of Examples 1 to 16 (3.5g) were dissolved in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1. In Table 2 below, Ink 1 contains the compound of Example 1, Ink 2 the compound of Example 2 and so on.

Preparation of the Comparative Ink

15 The compound of the Comparative Example (3.5g) was dissolved in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1.

Example 34

Ozone Fastness

20 The Example Inks 1 to 16 and the Comparative Ink were printed onto a variety of papers using a Canon 5800™ IJ printer. The printed substrate was then assessed for ozone stability using an ozone test cabinet from Hampden Test Equipment. The test was carried out for twenty four hours at 40°C and 50% relative humidity in the presence of 1 part per million of ozone. Fastness of the printed ink to ozone was judged by the difference in the optical density before and after exposure to ozone using a Gretag
25 MacBeth Spectrolino. Thus, the lower the %OD loss the greater the ozone fastness. Results are shown below in Table 2 and these clearly demonstrate that inks based on compounds of this invention display good ozone fastness.

Table 2

Ink	Substrate	% OD loss
Ink 1	HP Premium Plus	2
Ink 1	Canon PR101	48
Ink 1	SEC Premium Photo	53
Ink 2	HP Premium Plus	0
Ink 2	Canon PR101	27
Ink 2	SEC Premium Photo	21
Ink 3	HP Premium Plus	0
Ink 3	Canon PR101	27
Ink 3	SEC Premium Photo	12
Ink 4	HP Premium Plus	2
Ink 4	Canon PR101	53
Ink 4	SEC Premium Photo	54
Ink 5	HP Premium Plus	3
Ink 5	Canon PR101	52
Ink 5	SEC Premium Photo	45
Ink 6	HP Premium Plus	2
Ink 6	Canon PR101	39
Ink 6	SEC Premium Photo	38
Ink 7	HP Premium Plus	3
Ink 7	Canon PR101	30
Ink 7	SEC Premium Photo	28
Ink 8	HP Premium Plus	2
Ink 8	Canon PR101	33
Ink 8	SEC Premium Photo	33
Ink 9	HP Premium Plus	-1
Ink 9	Canon PR101	41
Ink 9	SEC Premium Photo	41
Ink 10	HP Premium Plus	2
Ink 10	Canon PR101	43
Ink 10	SEC Premium Photo	45
Ink 11	HP Premium Plus	1
Ink 11	Canon PR101	37
Ink 11	SEC Premium Photo	39
Ink 12	HP Premium Plus	4
Ink 12	Canon PR101	55

Ink 12	SEC Premium Photo	56
Ink 13	HP Premium Plus	3
Ink 13	Canon PR101	23
Ink 13	SEC Premium Photo	19
Ink 14	HP Premium Plus	0
Ink 14	Canon PR101	17
Ink 14	SEC Premium Photo	12
Ink 15	HP Premium Plus	1
Ink 15	Canon PR101	15
Ink 15	SEC Premium Photo	7
Ink 16	HP Premium Plus	2
Ink 16	Canon PR101	28
Ink 16	SEC Premium Photo	25
Comparative Ink	HP Premium Plus	4
Comparative Ink	Canon PR101	71
Comparative Ink	SEC Premium Photo	64

Further Inks

The inks described in Tables A and B may be prepared using the compounds made in Examples 1 to 16. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink-jet printing.

The following abbreviations are used in Table A and B:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

BDL = butane-2,3-diol

CET= cetyl ammonium bromide

PHO = Na_2HPO_4 and

TBT = tertiary butanol

TDG = thiodiglycol

TABLE A

Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2					
3	10.0	85	3		3	3				5	1	
4	2.1	91		8								1
5	3.1	86	5					0.2	4			5
6	1.1	81			9		0.5		6		9	
7	2.5	60	4	15	3	3			10	10	5	4
8	5	65		20								
9	2.4	75	5	4		5				6		5
10	4.1	80	3	5	2	10		0.3				
11	3.2	65		5	4	6			5	4	6	5
12	5.1	96		5						4		
13	10.8	90	5						5	4		
14	10.0	80	2	6	2	5			1		4	
15	1.8	80		5							15	
16	2.6	84			11						5	
14	3.3	80	2			10				2		6
15	12.0	90				7	0.3		3			
14	5.4	69	2	20	2	1					3	3
15	6.0	91			4						5	

TABLE B

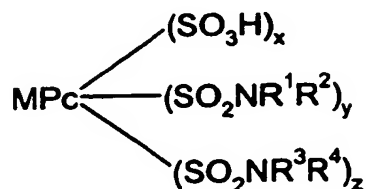
Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2						
2	9.0	90		5						1.2	5	5
3	1.5	85	5	5		0.15	5.0	0.2				
4	2.5	90		6	4					0.12		
5	3.1	82	4	8		0.3						
6	0.9	85		10								6
7	8.0	90		5	5			0.3	5	0.2		
8	4.0	70		10	4				1			
9	2.2	75	4	10	3				2		4	11
10	10.0	91			6						6	
11	9.0	76			7		3.0			0.95	3	
12	5.0	78	5	9							5	
13	5.4	86		11							6	
14	2.1	70	5	5	7						7	
15	2.0	90		10	5	0.1	0.2	0.1	5	0.1	5	
16	2	88										
14	5	78			5			10				
15	8	70	2		8			12			5	
14	10	80						15			5	
15	10	80		10				8			12	

CLAIMS

1. A process for forming an image on a substrate comprising applying a composition which comprises:

5

(a) a compound of Formula (1) and salts thereof:



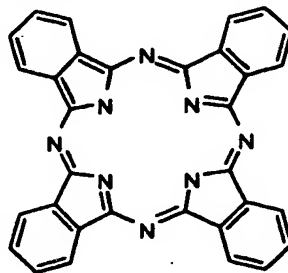
10

Formula (1)

wherein:

M is Cu or Ni;

Pc represents a phthalocyanine nucleus of Formula (2);



15

Formula (2)

R^1 , R^2 and R^3 independently are H or optionally substituted C_{1-4} alkyl;

R^4 is optionally substituted C_{1-4} -hydroxyalkyl;

20

x is greater than 0 and less than 1.8;

y and z are both greater than 0; and

the sum of (x+y+z) is 2.4 to 4.5; and

(b) a liquid medium:

thereto by means of an ink-jet printer.

25

2. A process according to claim 1 wherein in the compound of Formula (1) R^1 , R^2 and R^3 are all H.

3. A process according to either claim 1 or claim 2 wherein in the compound of Formula (1) R^4 is unsubstituted C_{1-4} -hydroxyalkyl.

30

4 A process according to any one of the preceding claims wherein in the compound of Formula (1) R^4 is C_2 -hydroxyalkyl.

5 5. A process according to any one of the preceding claims wherein in the compound of Formula (1) x is greater than 0 and less than 1.5.

6. A process according to any one of the preceding claims wherein in the compound of Formula (1) x is greater than 0 and less than 1.2.

10

7. A process according to any one of the preceding claims wherein in the compound of Formula (1) x is greater than 0.05 and less than 1.0.

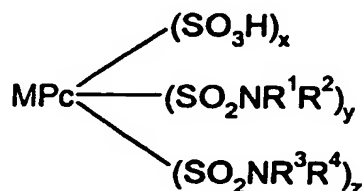
8. A process according to any one of the preceding claims wherein in the compound of Formula (1) x is greater than 0.05 and less than 0.5.

15

9. A composition comprising:

(a) a compound of Formula (1) and salts thereof:

20

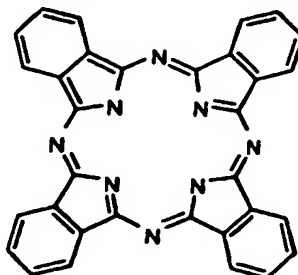


Formula (1)

wherein:

25

M is Cu or Ni;
Pc represents a phthalocyanine nucleus of Formula (2);



Formula (2)

30

R^1 , R^2 and R^3 independently are H or optionally substituted C_{1-4} alkyl;

R^4 is optionally substituted C_{1-4} -hydroxyalkyl;

x is greater than 0 and less than 1.8;

y and z are both greater than 0; and

5 the sum of $(x+y+z)$ is 2.4 to 4.5; and

(b) a liquid medium which comprises water and an organic solvent or an organic solvent free from water.

10 10. A composition according to claim 9 wherein in the compound of Formula (1) R^1 , R^2 and R^3 are all H.

11. A composition according to either claim 9 or claim 10 wherein in the compound of Formula (1) R^4 is unsubstituted C_{1-4} -hydroxyalkyl.

15 12. A composition according to claim 11 wherein in the compound of Formula (1) R^4 is C_2 -hydroxyalkyl.

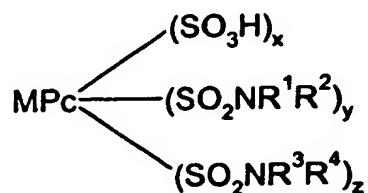
13. A composition according to any one of claims 9 to 12 wherein in the compound of Formula (1) x is greater than 0 and less than 1.5.

20 14. A composition according to claim 13 wherein in the compound of Formula (1) x is greater than 0 and less than 1.2.

25 15. A composition according to either claim 13 or claim 14 wherein in the compound of Formula (1) x is greater than 0.05 and less than 1.0.

16. A composition according to any one of claims 13 to 15 wherein in the compound of Formula (1) x is greater than 0.05 and less than 0.5.

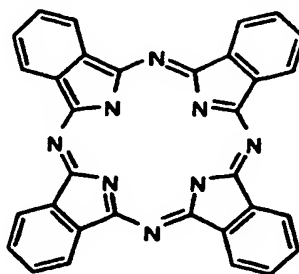
30 17. A compound of Formula (1) and salts thereof:



Formula (1)

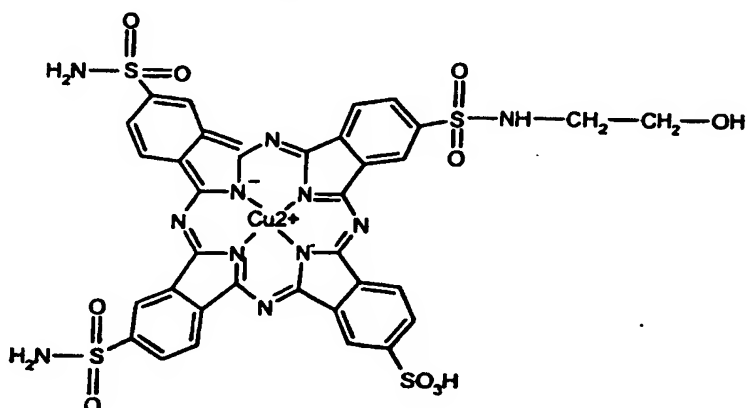
35 wherein:

M is Cu or Ni;
Pc represents a phthalocyanine nucleus of Formula (2);



Formula (2)

R^1 , R^2 and R^3 independently are H or optionally substituted C_{1-4} alkyl;
 R^4 is optionally substituted C_{1-4} -hydroxyalkyl;
 x is greater than 0 and less than 1.8;
 y and z are both greater than 0; and
the sum of $(x+y+z)$ is 2.4 to 4.5;
provided that the compound of Formula (1) is not of formula



18. A compound according to claim 17 wherein in the compound of Formula (1) R^1 , R^2 and R^3 are all H.

19. A compound according to either claim 17 or claim 18 wherein in the compound of Formula (1) R^4 is unsubstituted C_{1-4} -hydroxyalkyl.

20. A compound according to claim 19 wherein in the compound of Formula (1) R^4 is C_2 -hydroxyalkyl.

21. A compound according to any one of claims 17 to 20 wherein in the compound of Formula (1) x is greater than 0 and less than 1.5.
- 5 22. A compound according to claim 21 wherein in the compound of Formula (1) x is greater than 0 and less than 1.2.
23. A compound according to either claim 21 or claim 22 wherein in the compound of Formula (1) x is greater than 0.05 and less than 1.0.
- 10 24. A compound according to any one of claims 21 to 23 wherein in the compound of Formula (1) x is greater than 0.05 and less than 0.5.
25. A composition which comprises a compound of Formula (1) according to any one of claims 17 to 24 and a liquid medium.
- 15 26. A paper, plastic, textile, metal or glass material printed by means of a process according to any one of claims 1 to 8.
27. A paper, plastic, textile, metal or glass material printed with a composition according to any one of claims 9 to 16 or 25.
- 20 28. A paper, plastic, textile, metal or glass material printed with a compound according to any one of claims 17 to 24.
- 25 29. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in any one of claims 9 to 16 or 25.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 03/04035

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D11/00 C09B47/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 732 615 A (OTA MITSUHIRO ET AL) 22 March 1988 (1988-03-22) examples 6-14 column 3, lines 9-29 column 4, lines 24-27 column 7, line 51 - column 8, line 47; table 3	1,2,5,6, 9,10,13, 14,17, 18,21, 22,25-29
A	US 6 149 722 A (KENWORTHY MARK ET AL) 21 November 2000 (2000-11-21) cited in the application claim 1; examples 1,2	1-29
A	US 5 704 969 A (KANAYA MIHARU ET AL) 6 January 1998 (1998-01-06) claim 1	1-29

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

14 January 2004

Date of mailing of the international search report

21/01/2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 03/04035

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4732615	A	22-03-1988	EP 0196901 A2 JP 62149758 A	08-10-1986 03-07-1987
US 6149722	A	21-11-2000	AT 247693 T AU 4278999 A CN 1116364 B DE 69910581 D1 EP 1239010 A1 EP 1093492 A1 WO 9967334 A1 JP 2002522561 T TW 538104 B	15-09-2003 10-01-2000 30-07-2003 25-09-2003 11-09-2002 25-04-2001 29-12-1999 23-07-2002 21-06-2003
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